Nano-structural Thermal Materials Design for Transport and Energy Harvesting

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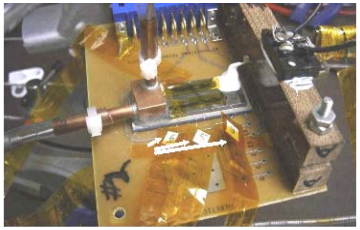
Thermal Loads Are Rising Sharply

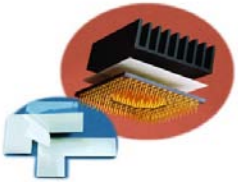
- Thermal load in satellites is doubling in every 5.5 years
- Space Structures
  - Heat flux of 700 W/cm^2 (hot spots by actuators, etc.)
    - To spread the hot spots (ΔT~1°C across Δx~1cm) requires material of thermal conductivity of κ~70 W/m-K
    - In comparison κ for adhesive ~ 0.3 W/m-K
- Electronics Cooling
  - κ_z ~ 60-70 W/m-K is desirable for Electronics Heat Sink system
- Need for high fidelity thermal component design for tailoring its thermal properties to meet system requirements

Heat pipe

Heat exchanger



Electronic cooling



Heat Sink Interface

Management of Thermal Energy in Materials & Systems

Thermal Energy Mgmt

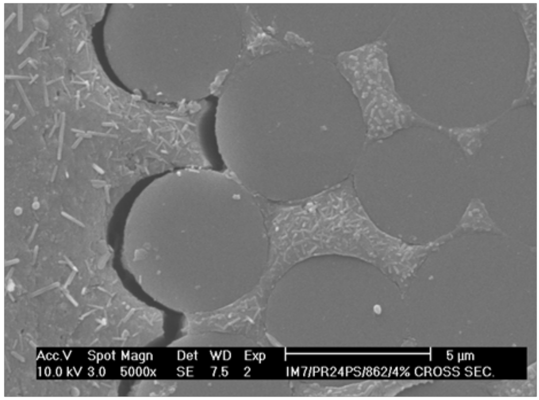
- Thermal transport in materials and system components
- Thermal energy storage
- Thermal energy conversion
- Etc.

Technical Approaches

- Passive system (tailoring material thermal properties)
- Active system (micro porous heat fluid flow, etc.)
- Etc.

Thermal materials & its interface property tailoring

Technical Challenge



- Numerous prior efforts have been made by mixing of CNT in polymers (epoxy) yields limited improvement in thermal conductivity (κ)
- κ (SWNT) ~ 2000 – 6000 W/m-K
- Improvement is limited to only 125% (κ ~ 0.7 W/m-K)

M. J. Biercuk, et al, Apply. Phys. Lett., 80, 2767 (2002)

Primary reason of the limited improvement

- Phonon scattering at the CNT-polymer interface

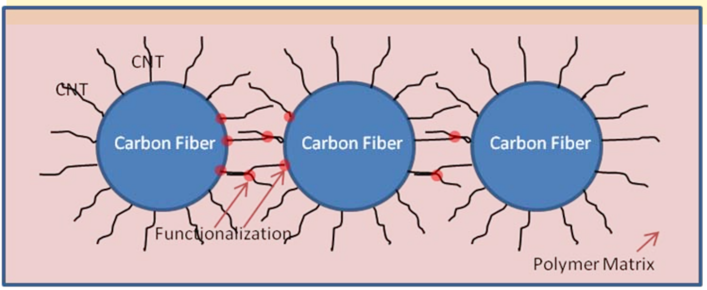
Technical Challenge

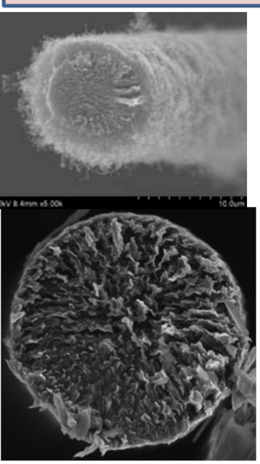
- Thermal interface design for aerospace materials
  - Nano constituents interface in presence of amorphous materials (composites and adhesive joints, etc.)

Two Examples of Thermal Materials Design for Aerospace Systems

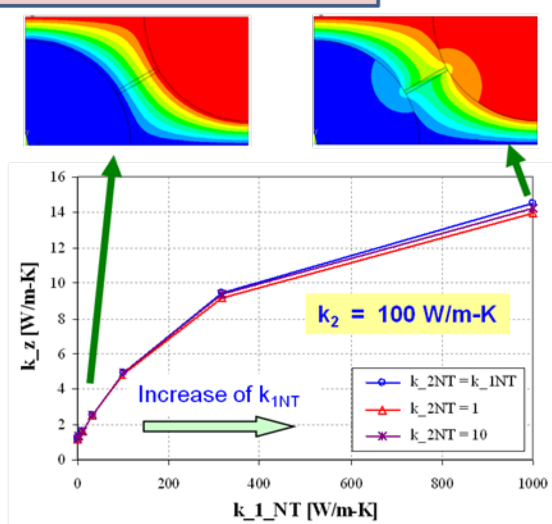
Hybrid Fiber Composites

- Intermingled network of Nano platelets grown on carbon fibers – embedded in polymer





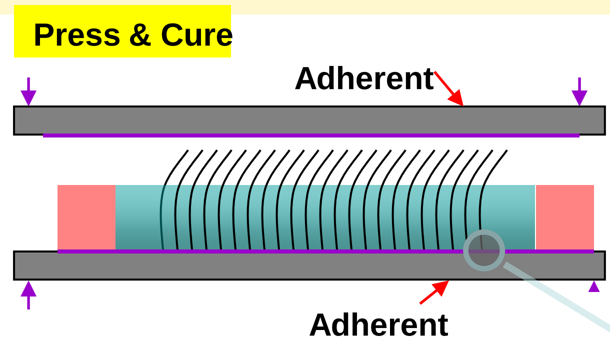
Pitch fiber



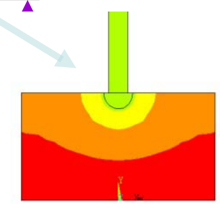
Roy, et al., Diamond & Related Materials, 2009

Aligned CNTs in adhesive joints

- Incorporation of MWNTs along the thickness of the adhesive joint



FEM modeling revealed need for establishing a conductive transition zone between MWNT and adherents



Thermal interface tailoring is essential for enhancing thermal conductivity in heterogeneous materials

Outline

- **Molecular dynamics simulation of thermal transport in cross-linked polymers**
- **Comparison of various energy components in polymer thermal transport**
- **Thermal interface resistance of CNT/polymer interface**
- **Thermal property measurement**
  - **Characterization tools under development**
  - **EELS technique**
  - **Micro heater**

Heat Transport Modeling of Epoxy Networks

Calculation of Thermal Conductivity

Green-Kubo Approach (Equilibrium MD): *This approach uses concept of* ***fluctuation-dissipation theorem*** *which relates equilibrium fluctuations to out of equilibrium properties via an* ***autocorrelation function***

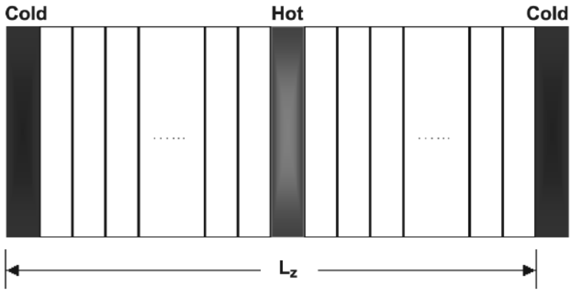
$$J(t) = \frac{1}{2}\sum_i \left[m_i v_i^2 + \sum_{j\neq i} u(r_{ij}) \right] \vec{v}_i + \frac{1}{2}\sum_{i,j\neq i} \vec{r}_{ij}\left(\vec{F}_{ij}^{R} \bullet \vec{v}_i \right) + \frac{1}{2}\sum_{i,j} \overleftrightarrow{S}_{ij}^{\alpha\beta} \bullet \vec{v}_i$$

$$\lambda = \frac{1}{k_B T^2 V}\int_0^\infty \langle J(t) \bullet J(0) \rangle dt$$

Fourier Approach (Non-Equilibrium MD): *This approach, also known as direct method, is analogus to experimental measurement. It is based on the principle that heat flux at certain cross-section is directly proportional to temperature gradient at that surface.*

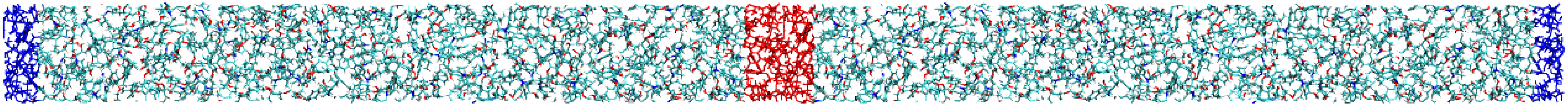
dT/dx = Temperature gradient
dQ/Adt = Heat flux per unit area per unit time

$$\lambda = \frac{dQ/dt}{A \times {}^{dT}\!/_{dx}}$$

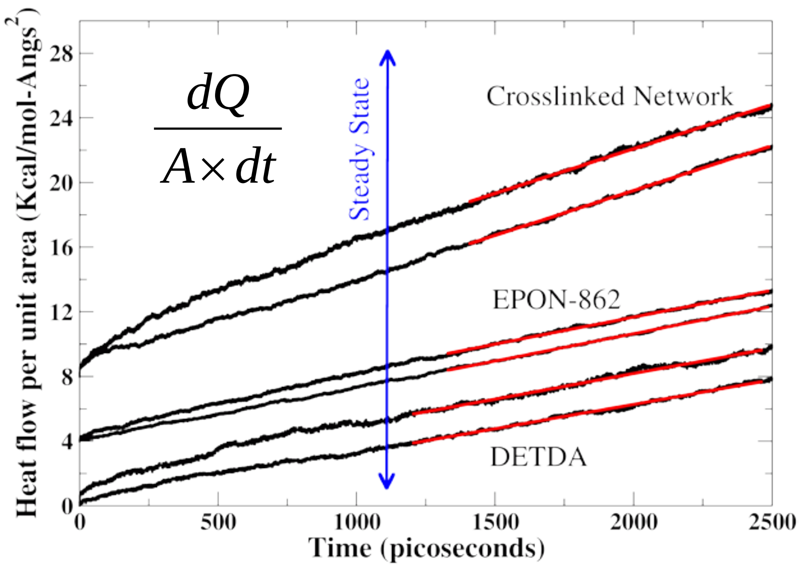


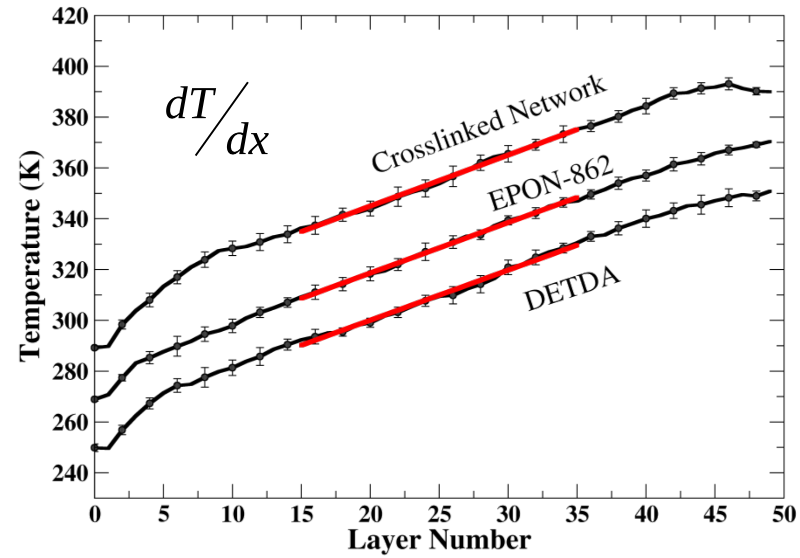
NEMD Simulations: Thermal Conductivity

Cold Region ***Hot Region*** ***Cold Region***



$$\lambda = \frac{dQ/dt}{A \times dT/dx}$$

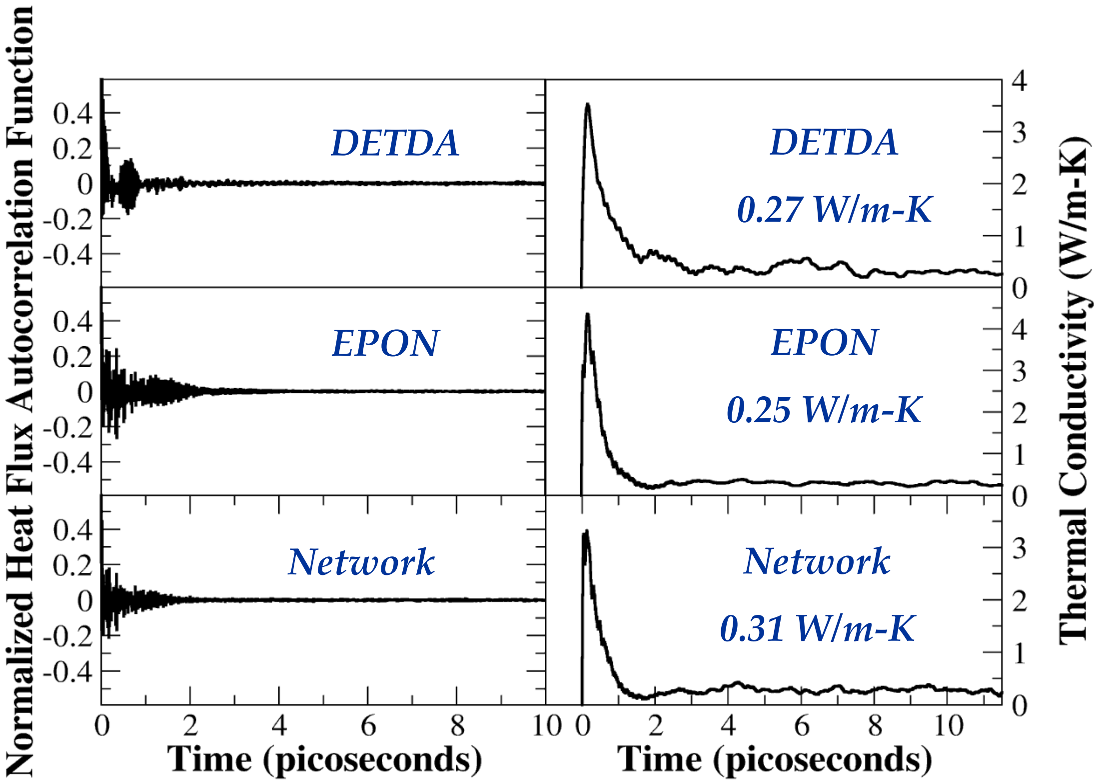




Thermal conductivity of the crosslinked network was found to be ~0.3 W/m-K which is in nice agreement with experimental findings.

EMD Simulations: Thermal Conductivity

$$\lambda = \frac{1}{k_B T^2 V} \int_0^\infty \langle J(t).J(0) \rangle dt$$



Comparison between both approaches

Material	Thermal Conductivity (W/m-K)	
	Green –Kubo Formalism	Fourier Law Formalism
DETDA	0.27	0.20
EPON-862	0.25	0.20
Crosslinked System	0.31	0.30

Experimental values of thermal conductivity of epoxy networks is ~0.28 W/m-K.

Energetic Contributions to Thermal Conductivity

1 2, 3 4, 5, 7, 8 6

$$\mathbf{J}(t) = \frac{1}{2}\sum_{i=1}^{N}\left[m_i v_i^2 + \sum_{j\neq i}^{N} u(r_{ij})\right]\mathbf{v}_i + \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}(\mathbf{r}_{ij}\mathbf{F}_{ij}^{R})\bullet\mathbf{v}_i + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\mathbf{v}_i \bullet \overleftrightarrow{\mathbf{S}}_{ij}$$

1: Contribution due to kinetic energy;

2, 3: Contribution due to potential energy (vdwl and electrostatic), respectively

4, 5: Contribution due to short range forces (vdwl and electrostatic), respectively

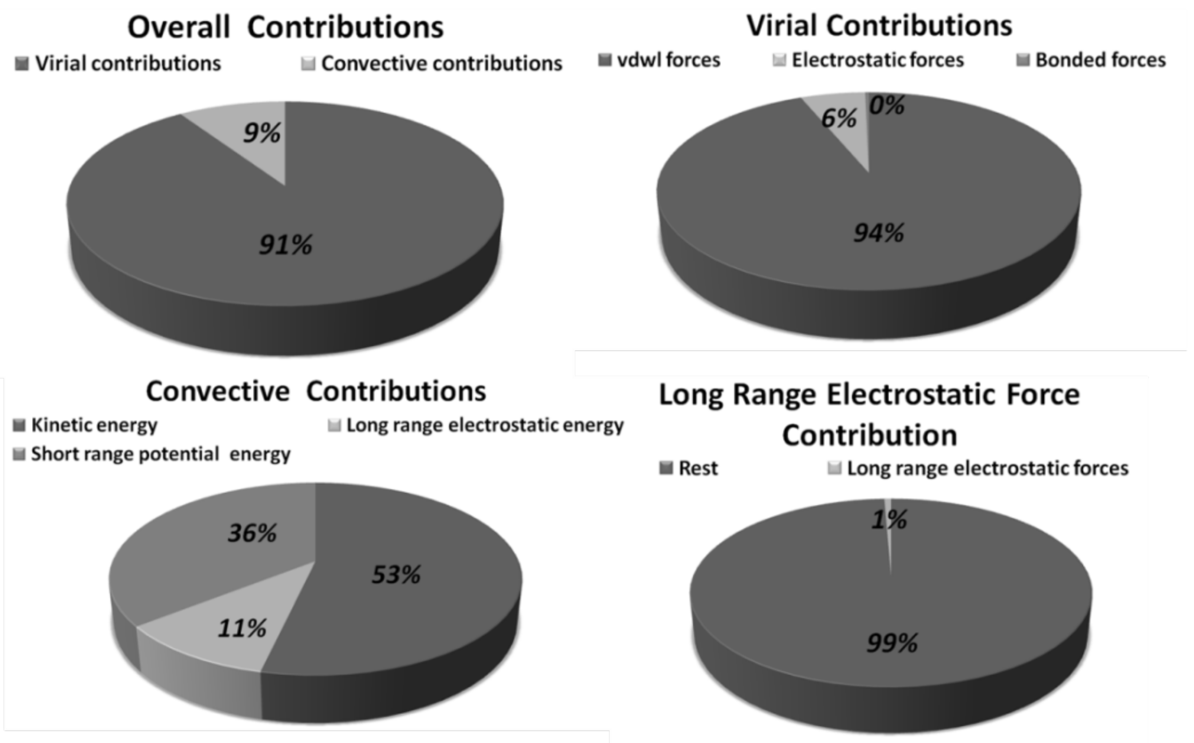
6: Contribution due to long range forces (electrostatic interactions: Ewald Sum)

7, 8: Contribution due to bonded interactions (bond stretching and angle bending)

Terms 1, 2 and 3 are known as Convective contributions.

Rest of them are known as Virial contributions.

Energy Contribution Analysis



Virial (collision) contribution is significantly larger than convective terms.

Van der Waals interaction and corresponding forces are the dominant contributors for thermal transport in polymers.

Electrostatic and bonded contributions are negligible.

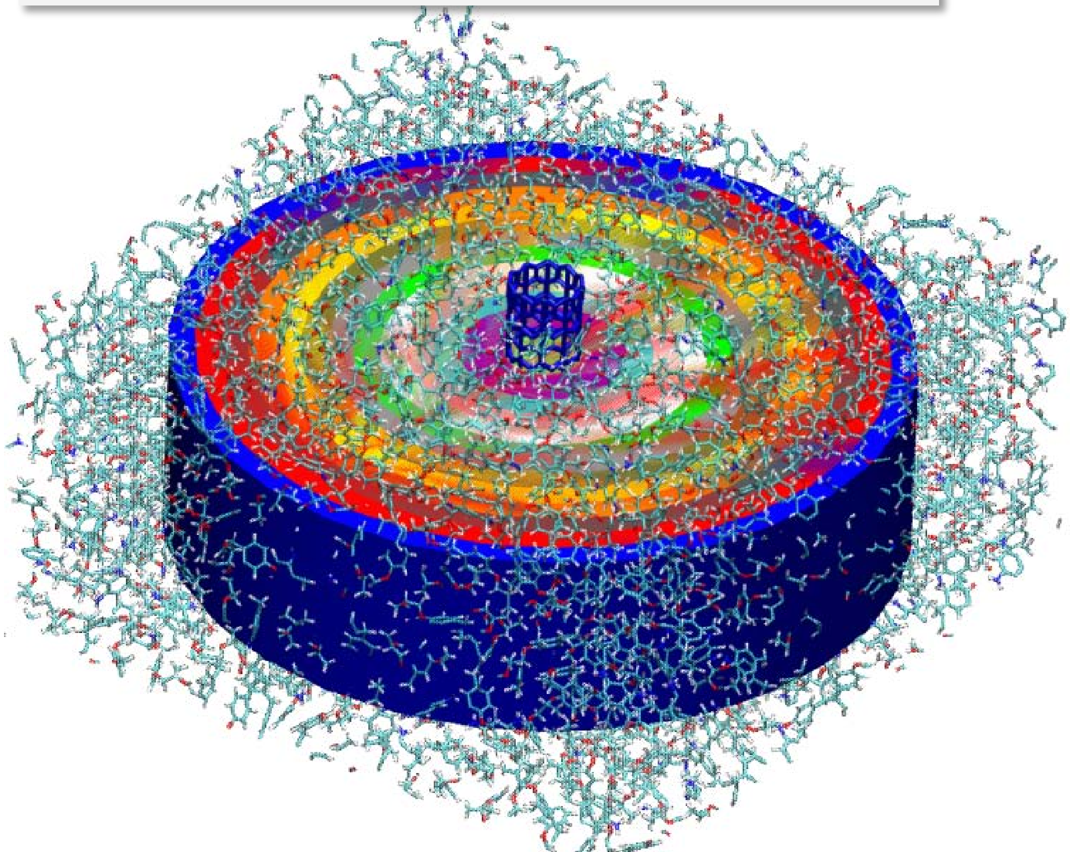
Interface Thermal Conductance at CNT Epoxy Interfaces.

System Studied

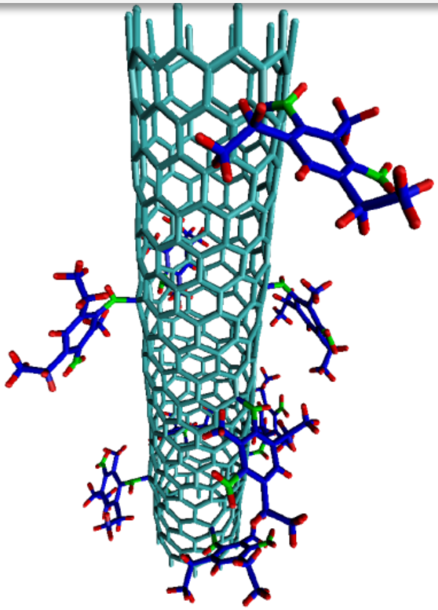
Heat Input at the constant rate in to CNT in the center

Heat Extraction from the outermost depicted (Blue) shell

We have used previously discussed algorithm (with minor alterations) to build shown nano-composite system with functionalized nanotubes.



Nanotube functionalized with DETDA



$$\Lambda = Q_{HeatFlux} / \Delta T_{Interface}$$

Systems Studied

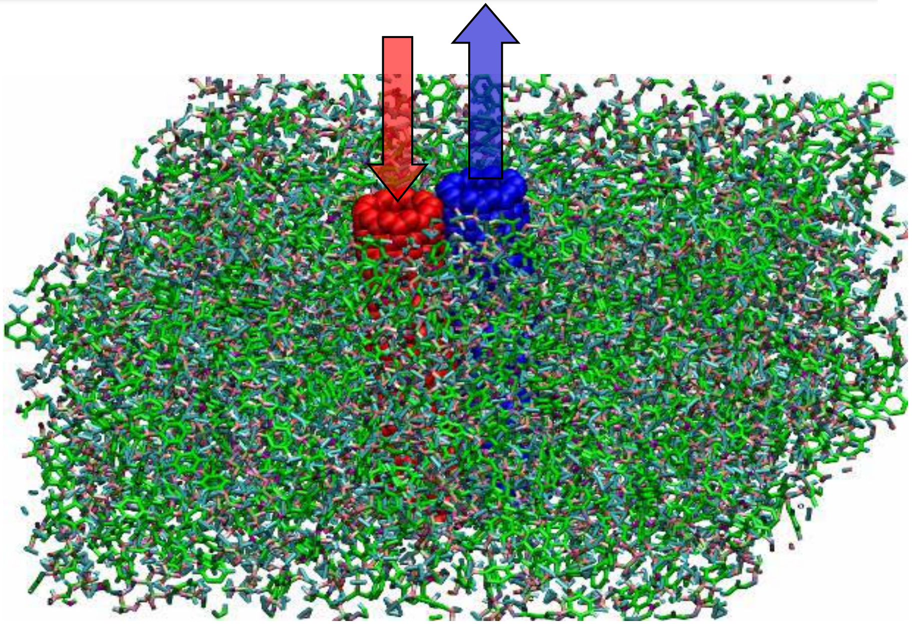
$$\Lambda = Q_{\text{Heat Flux per unit length}} / \Delta T_{\text{Interface}}$$

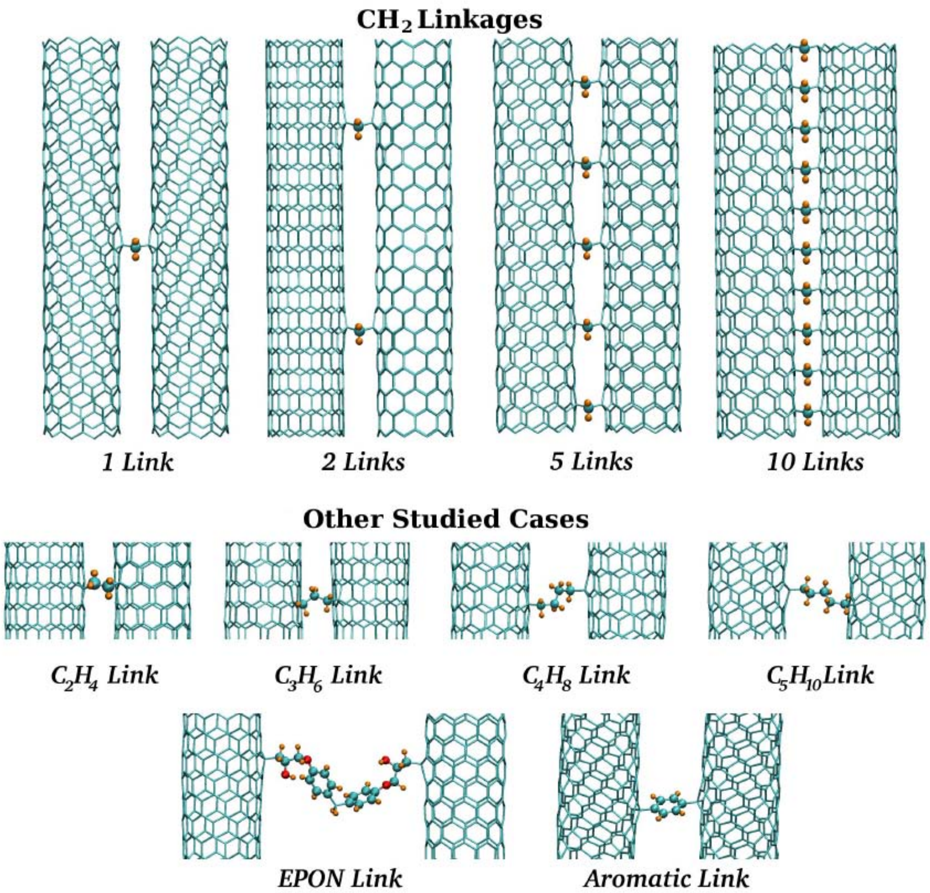
The arrow depicted the direction of heat flow.

Two types of simulations were performed.

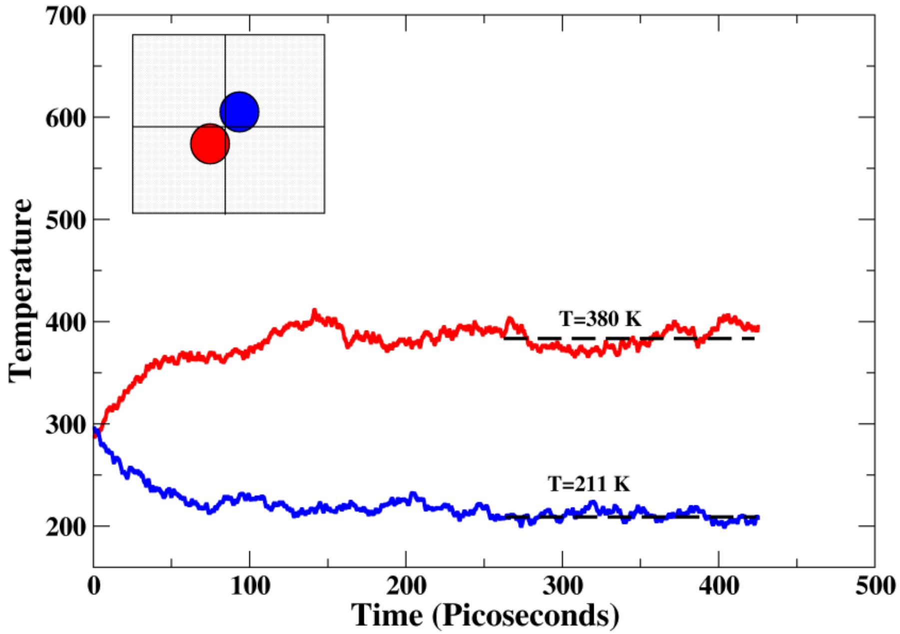
a) Epoxy-freezed

b) Epoxy-moving

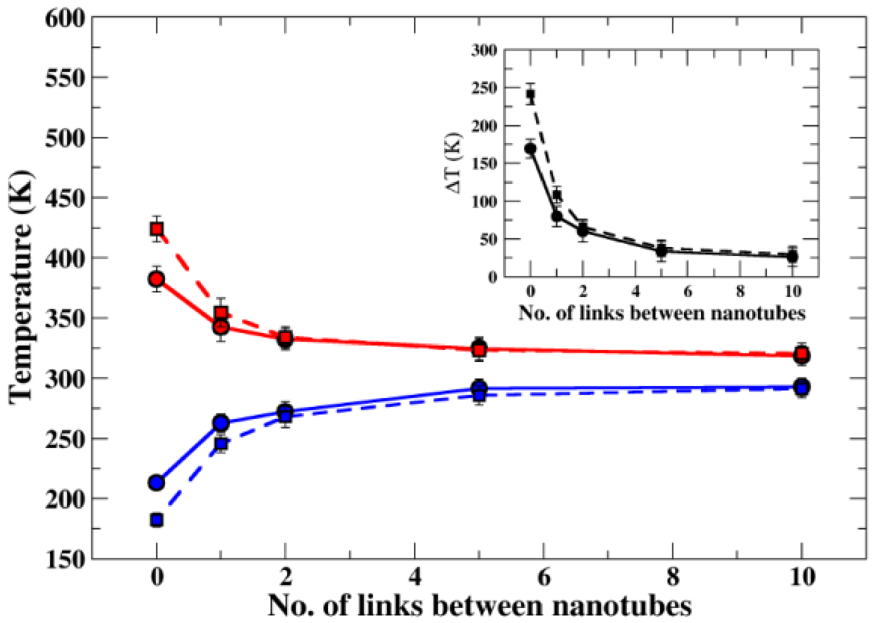




Results



Temperature evolution



Steady state temperatures vs. CH_2 linkages

Red: Temp. evolution of hot nanotube
Blue: Temp. evolution of cold nanotube.

The orientation of nanotubes with respect to system dimensions (top view) is schematically shown in the inset.

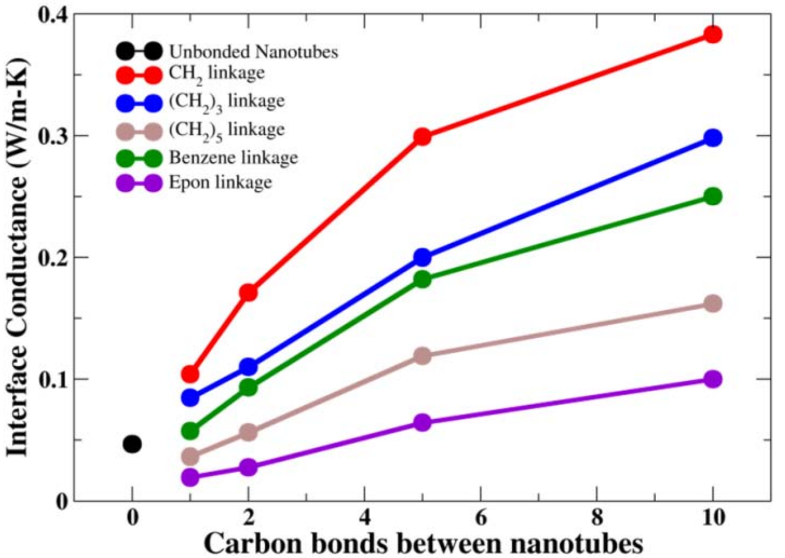
Solid Lines: Epoxy Moving simulations
Dashed Lines: Epoxy Freezed simulations

Inset shows the temperature drop between the two nanotubes as the function of CH_2 linking.

Interface Thermal Resistance across CNTs: Transverse Connection

Table 1: Comparison of Interface Thermal Resistance

Literature Studies	Thermal Interface Resistance (m^2-K/W)
Gao *et al.* (CNT-oil/polymer)	1.58×10^{-8} (Theoretical)[40]
Foygel *et al.*	10^7–10^8 K/W (Theoretical)[38]
Bryning *et al.* (CNT-Epoxy)	0.24-2.6 $\times 10^{-8}$ (Experimental)[41]
Huxtable *et al.* (CNT-water suspensions)	8.3×10^{-8} (Experimental)[11]
Cola *et al.*	0.2-7 $\times 10^{-8}$ (Experimental)[19]
Huxtable *et al.* (CNT-octane)	4.0×10^{-8} (Simulation)[11]
Shenogin *et al.* (CNT-octane)	3.3×10^{-8} (Simulation)[21]
Clancy *et al.* (CNT-polymer)	0.2-9.6 $\times 10^{-8}$ (Simulation)[23]
Carlborg *et al.* (CNT-argon)	40.0, 62.5 $\times 10^{-8}$ (Simulation)[25]
Murayama *et al.*	6.5×10^{-8} (Simulation)[42]
Zhong *et al.*	3.0-12.0 $\times 10^{-8}$ (Simulation)[26]
Xu *et al.*	0.01–0.5 $\times 10^{-8}$ (Simulation)[27]
Current Study	0.7–2.9 $\times 10^{-8}$ (Simulation)



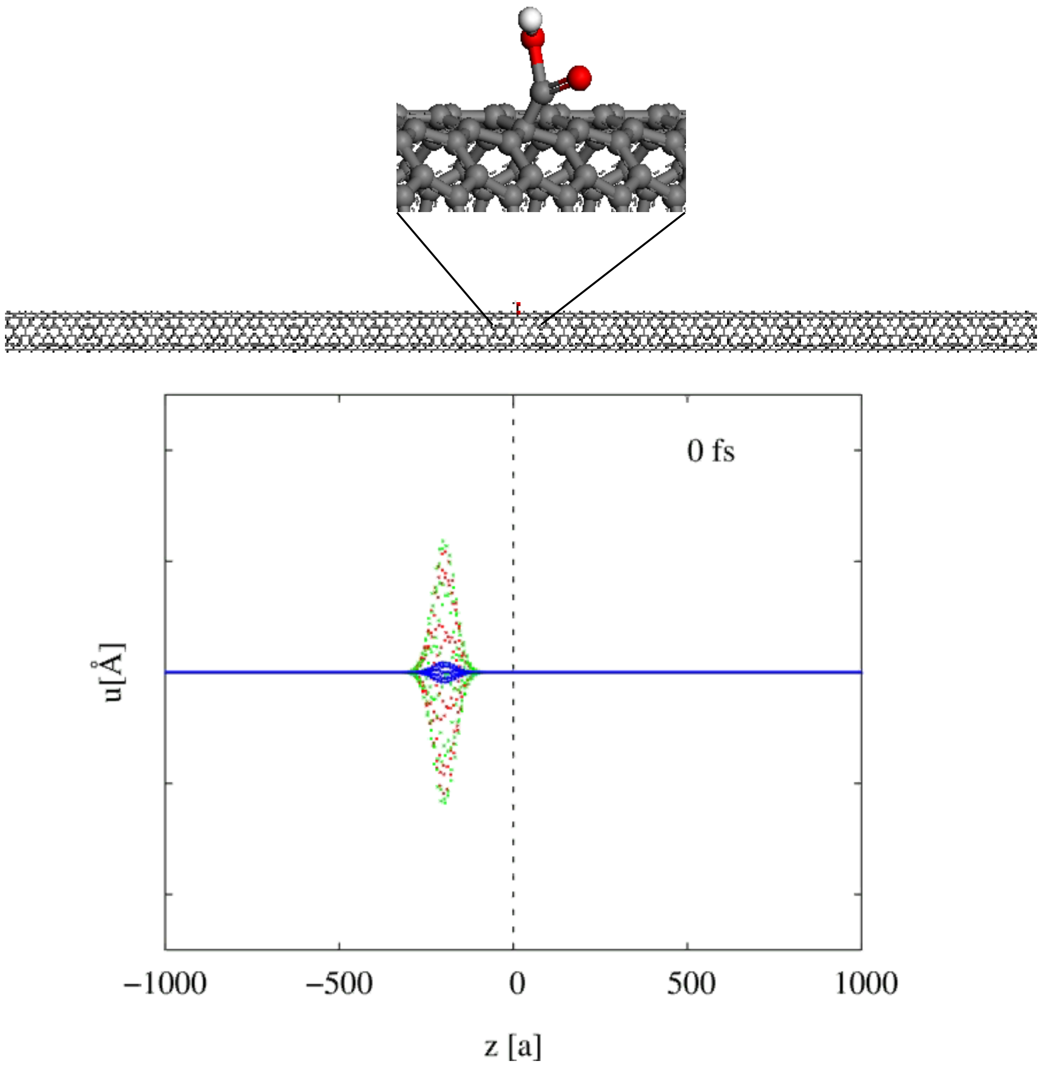
Effect of linkage length as well as their no. on overall interface conductance

Interface conductance increase with number of linkages but decreases with overall linker-length.

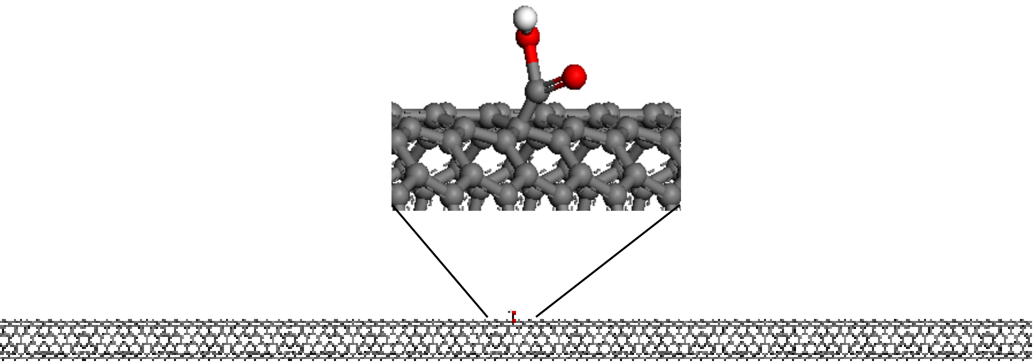
The deviation from linearity at higher degree of functionality is attributed to the inter-linkages interactions.

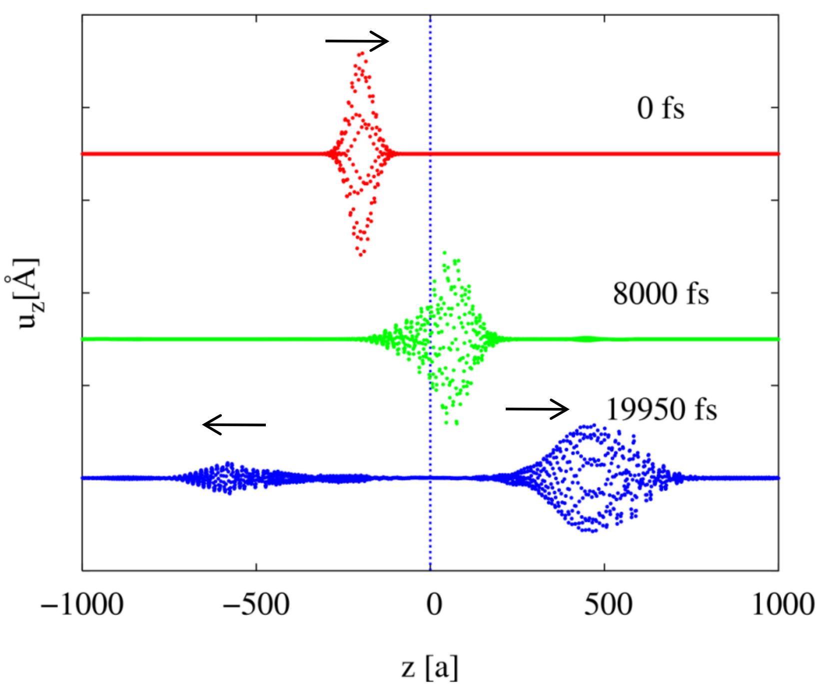
Two predicted values in the table are based on use of two different surface widths for cross-sectional areas consideration. a) 3.4 Angs and b) Nantube diameter.

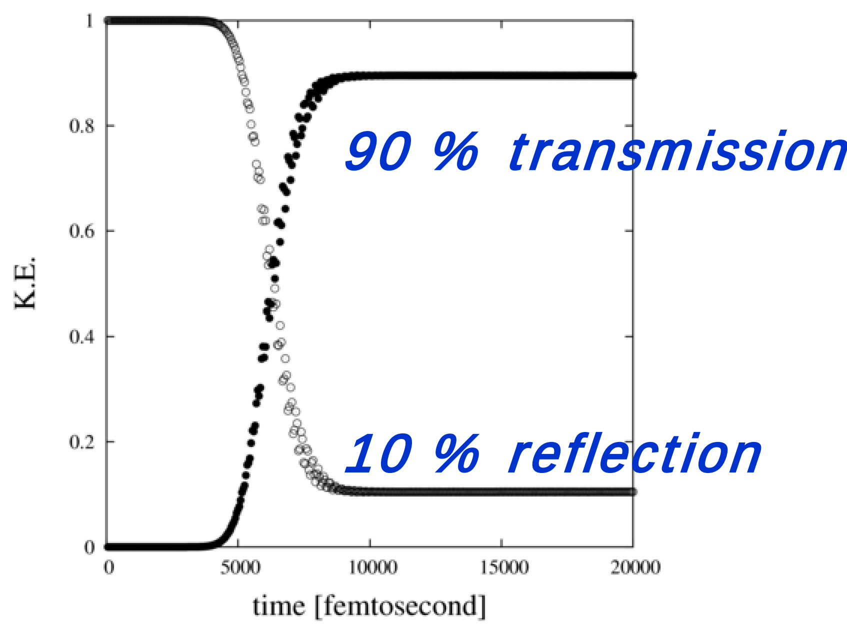
Wave Packets Analysis



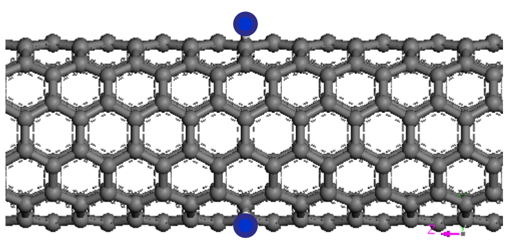
How to measure the energy transmission

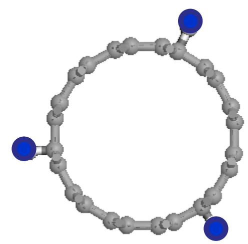






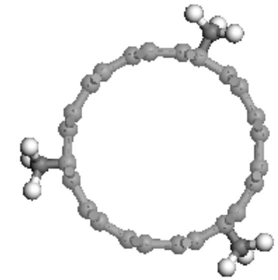
Single mode phonon transmission in functionalized CNT



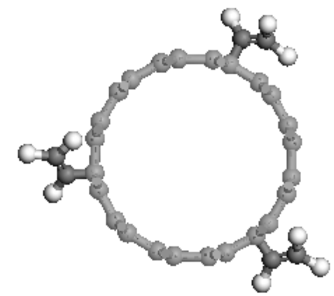


1. Effect of the functionalization on the phonon energy transmission.

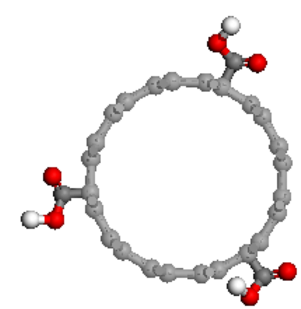
2. Effect of the difference in the functional group ….



$-CH_3$
(16 u)

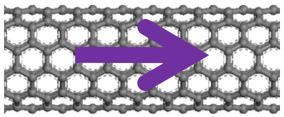


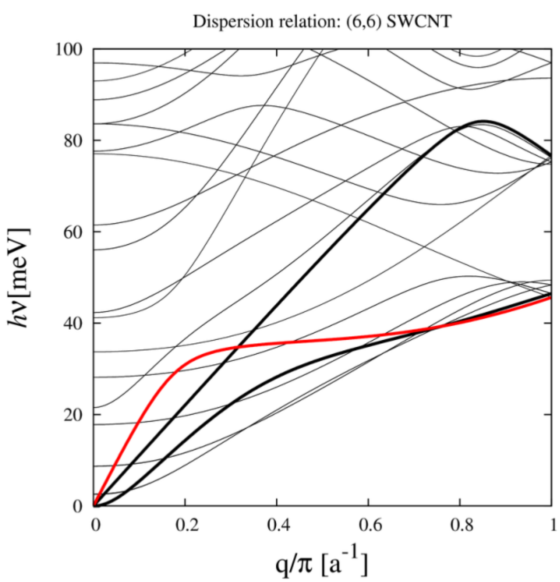
$-C_2H_3$
(27 u)

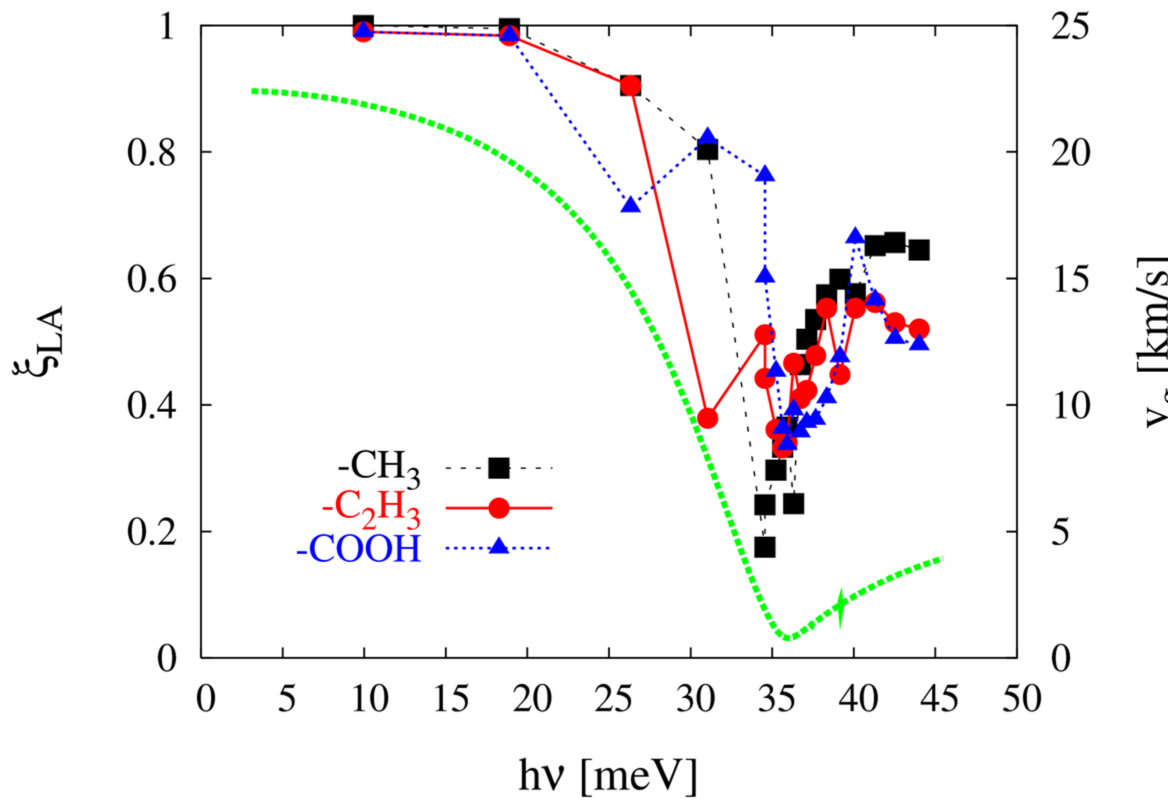


-COOH
(45 u)

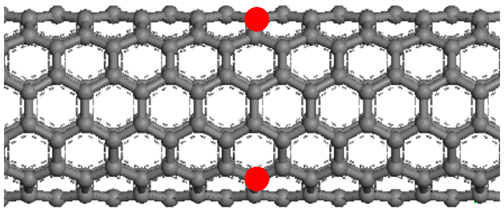
Longitudinal Acoustic mode

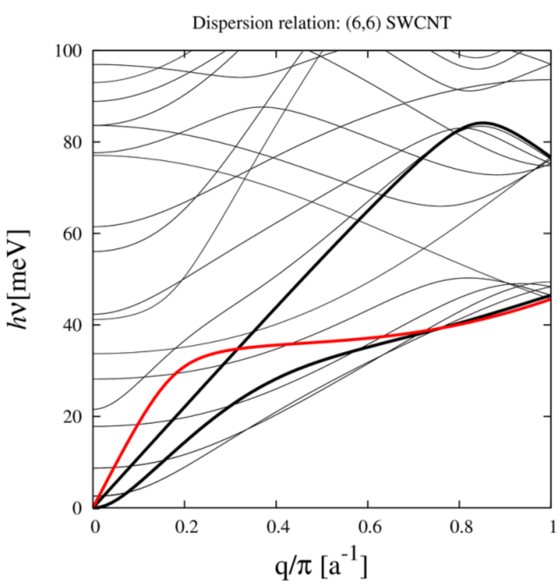


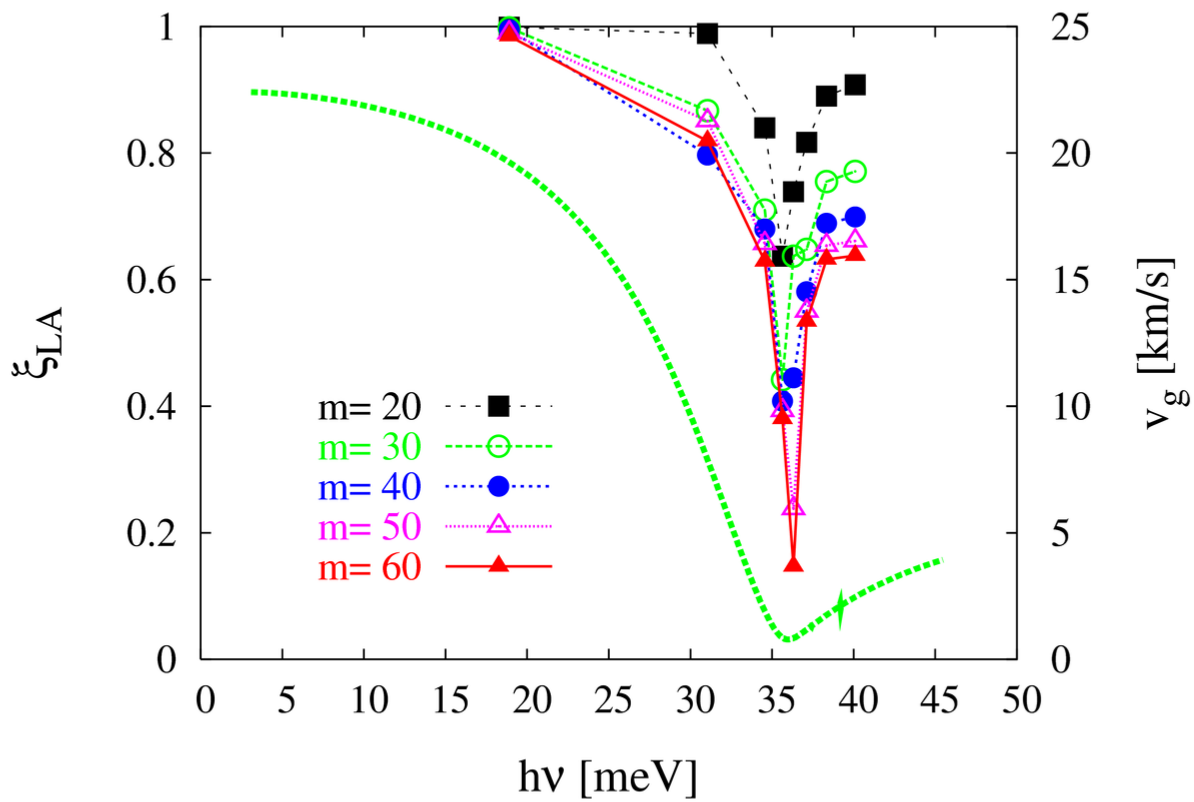




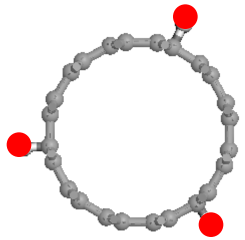
Point Mass defects: Longitudinal Acoustic mode

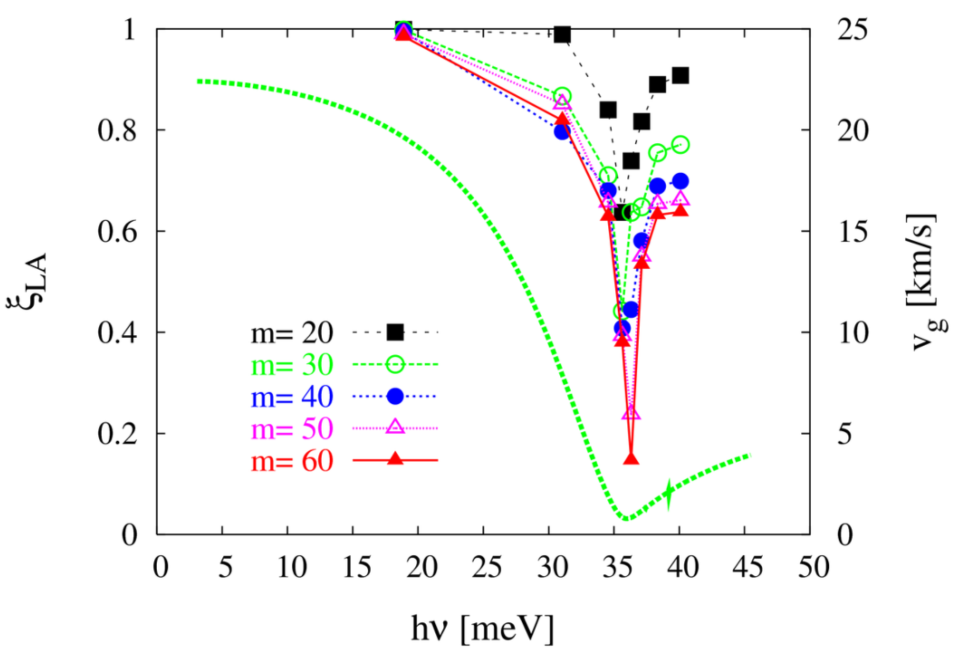


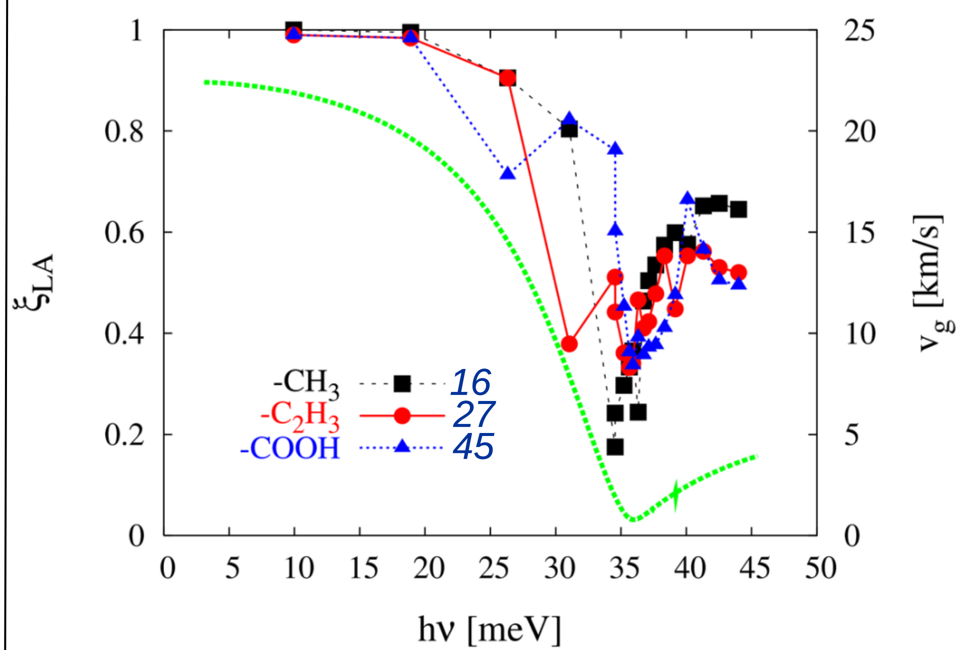




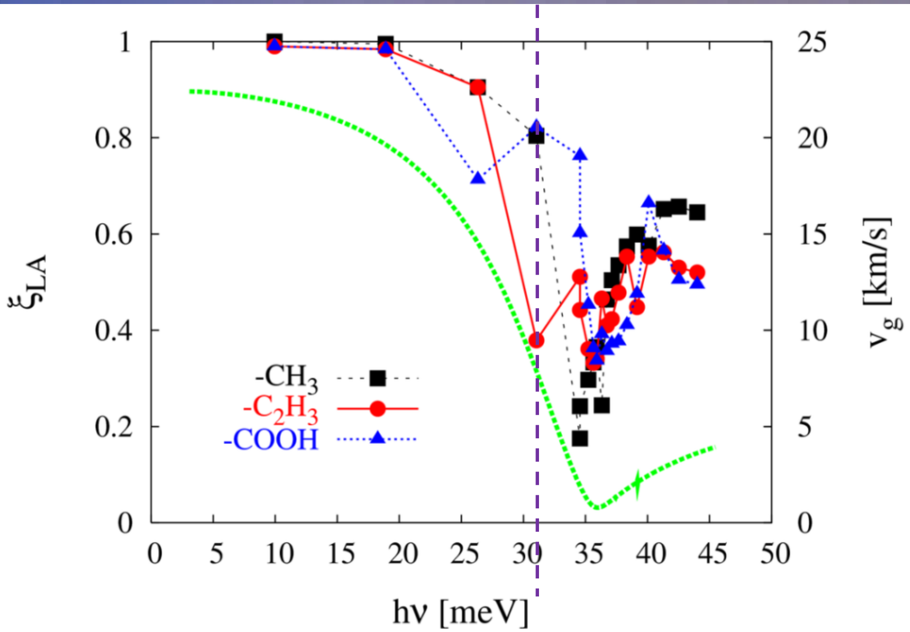
Group velocity effect: Longitudinal Acoustic mode

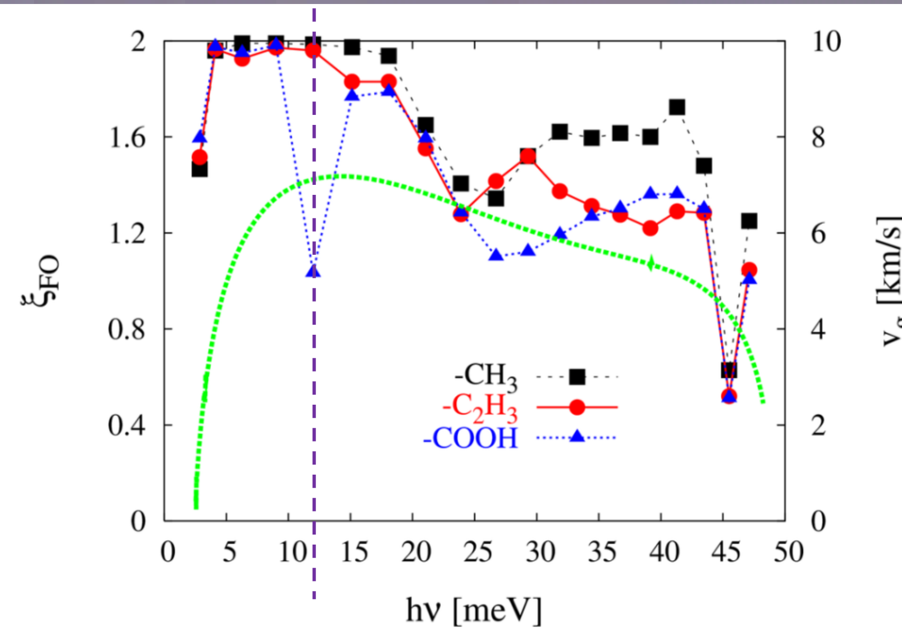


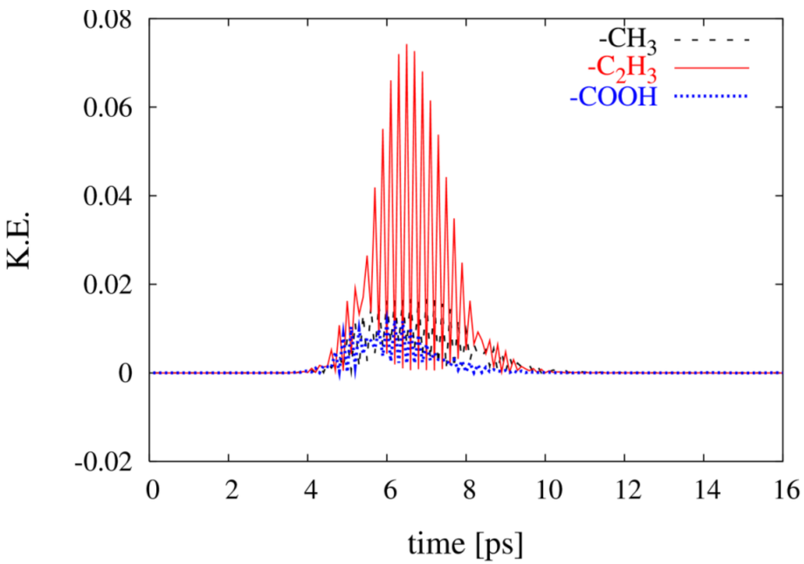


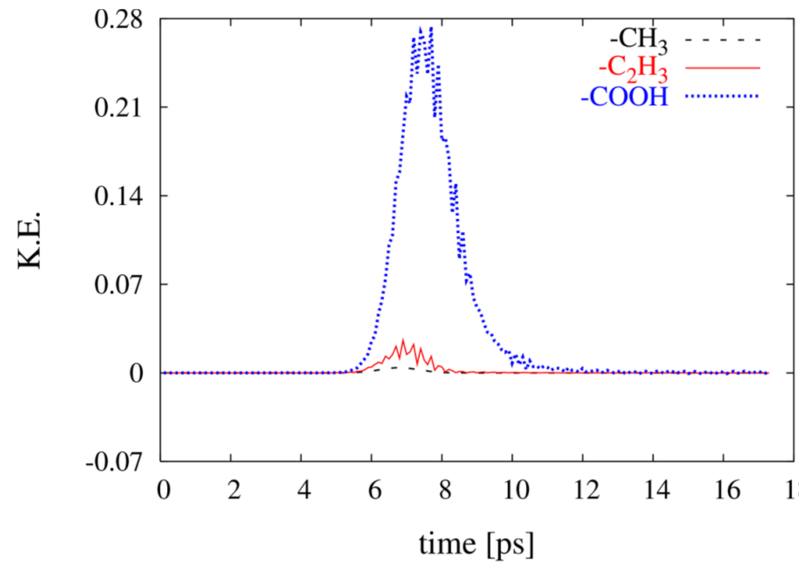


Coupling to the functional group

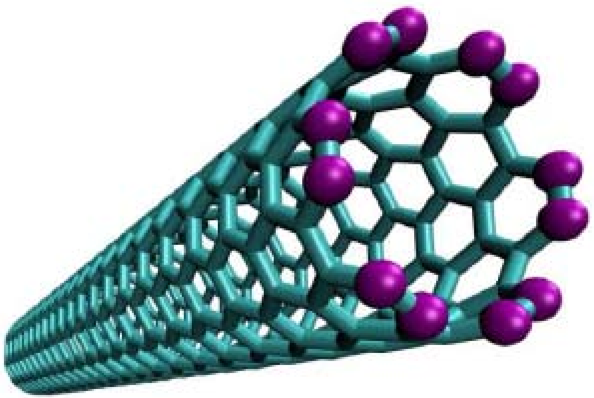




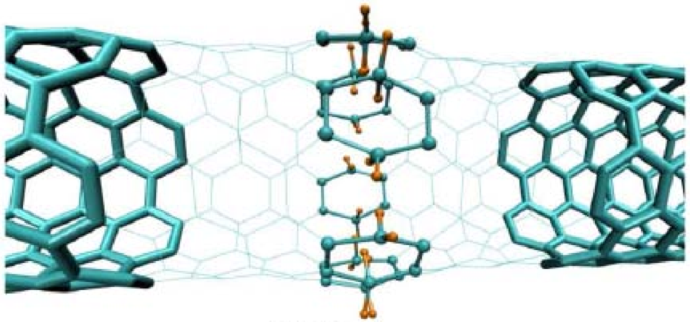




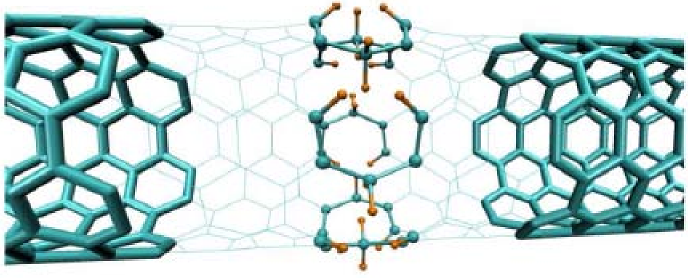
CNT with vertical $-CH_2$ linkers



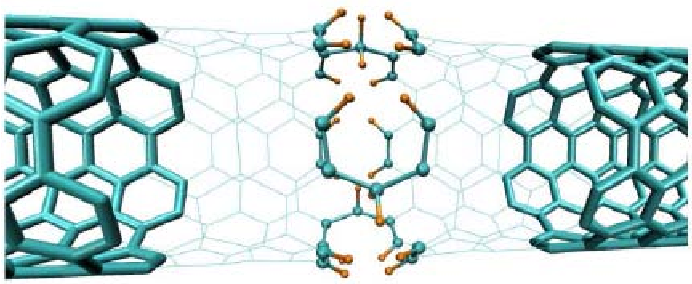
Cross-section of (6,6) nanotube



12 linkages



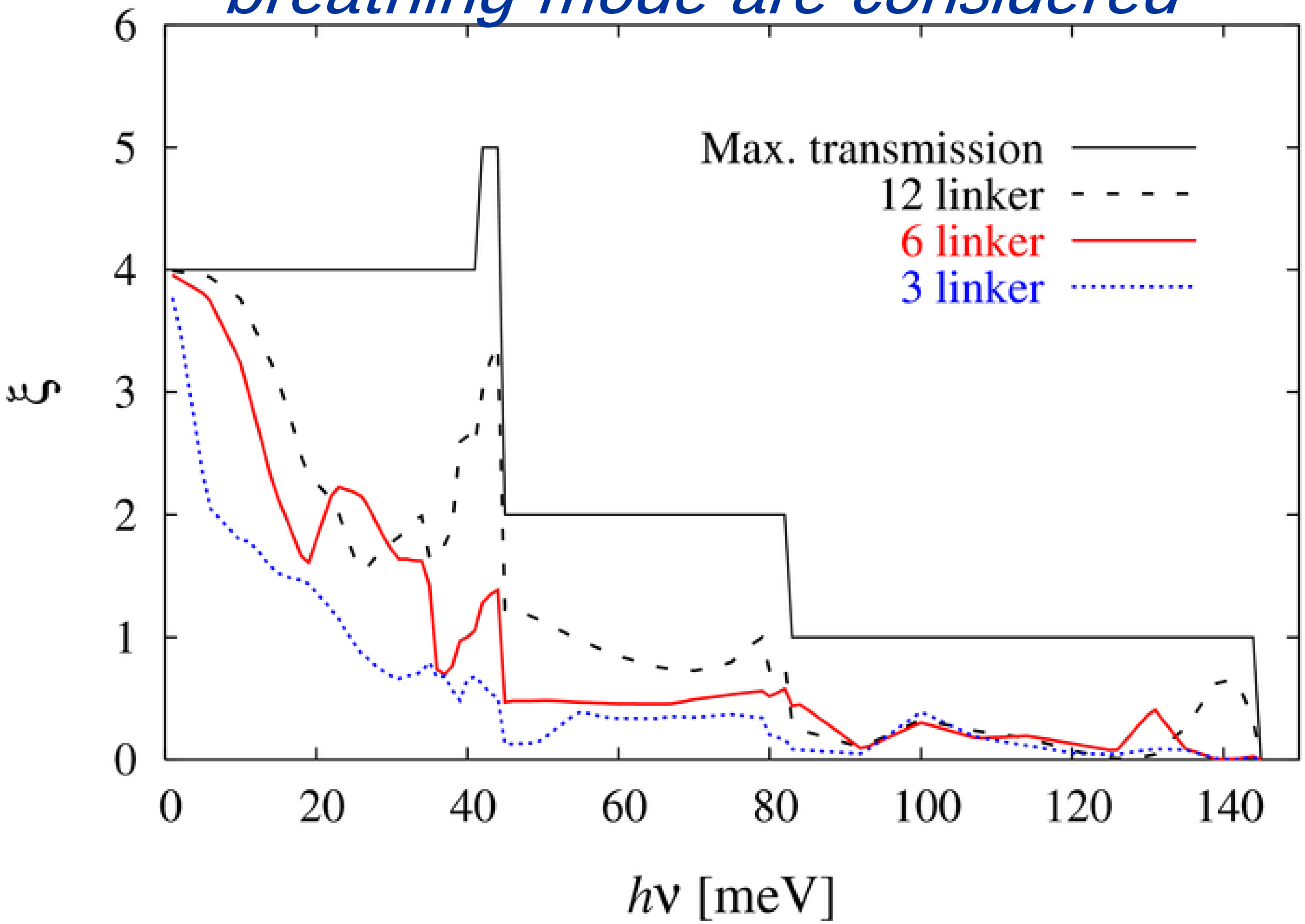
6 linkages



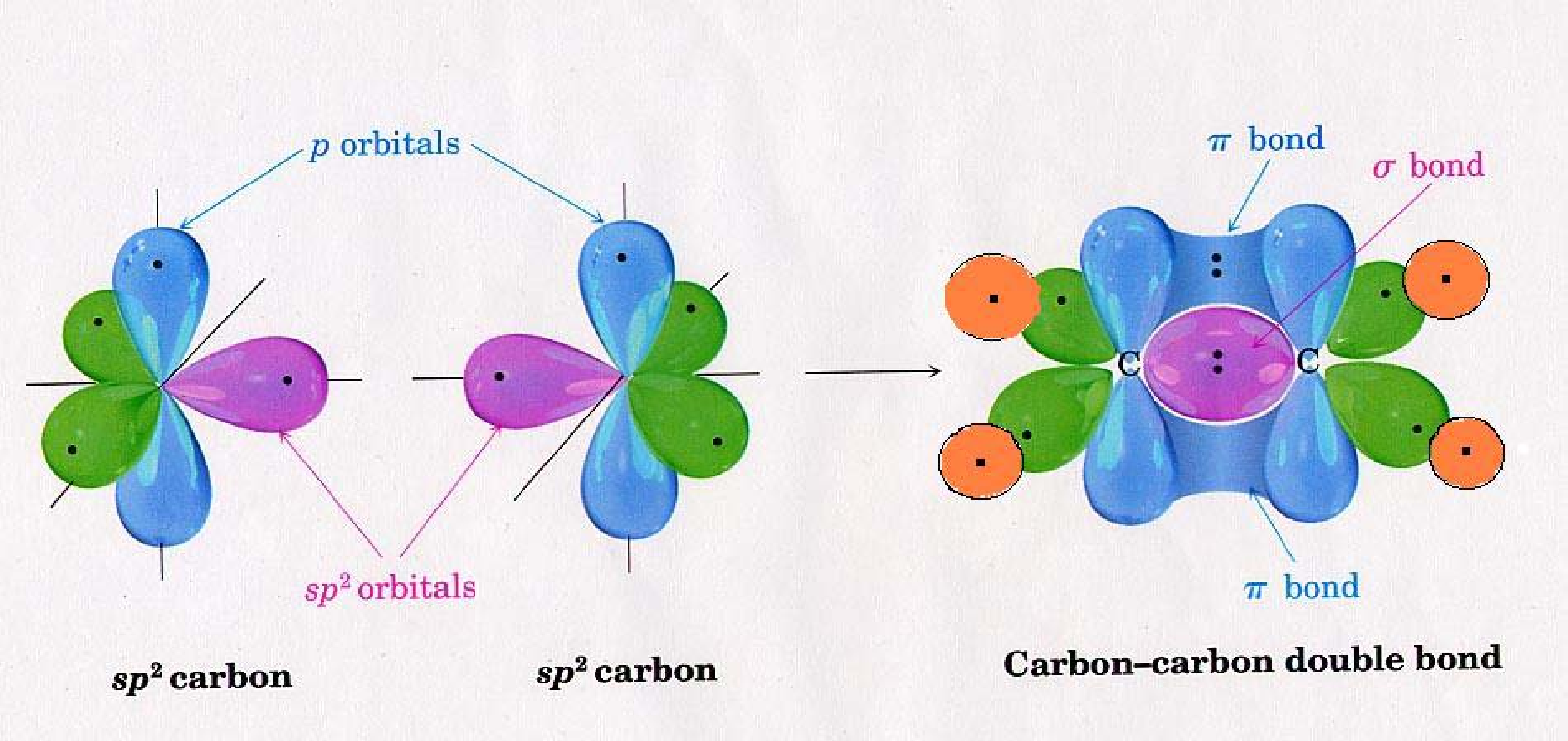
3 linkages

Phonon Energy Transmission in CNT with vertical links

- 4 Accoustic polarizations and the radial breathing mode are considered



Electron Emission Loss Spectroscopy (Orbital Picture of Ethylene)



http://www.uaf.edu/chem/green
Chapter1McMurry.ppt

EELS Spectrum Analysis

- pi – pi* transition
- sigma – sigma* transition
- pi - sigma* interbrand transition
- sigma - pi* interbrand transition
- In HOPG

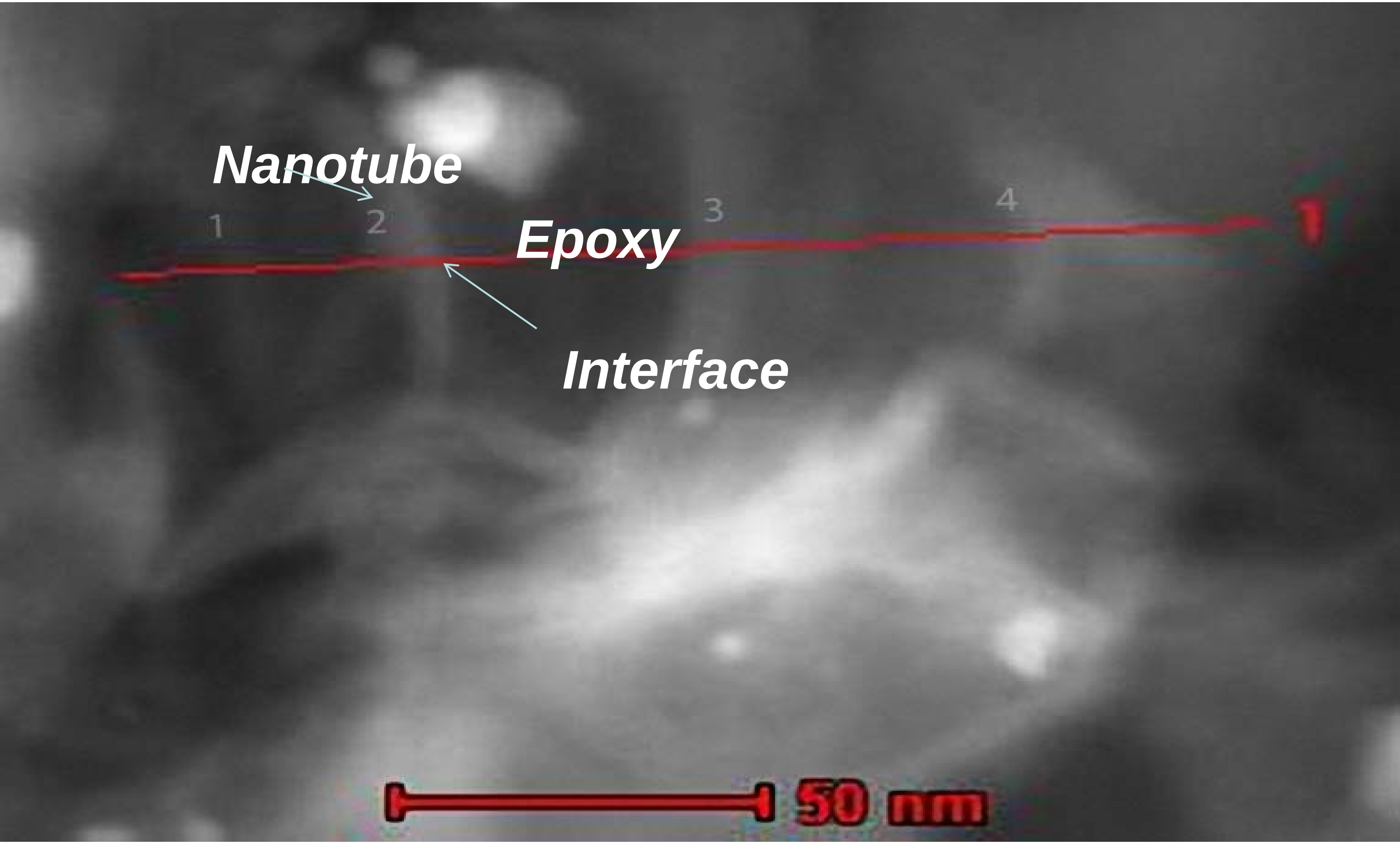
  pi transition - ~ 6 eV

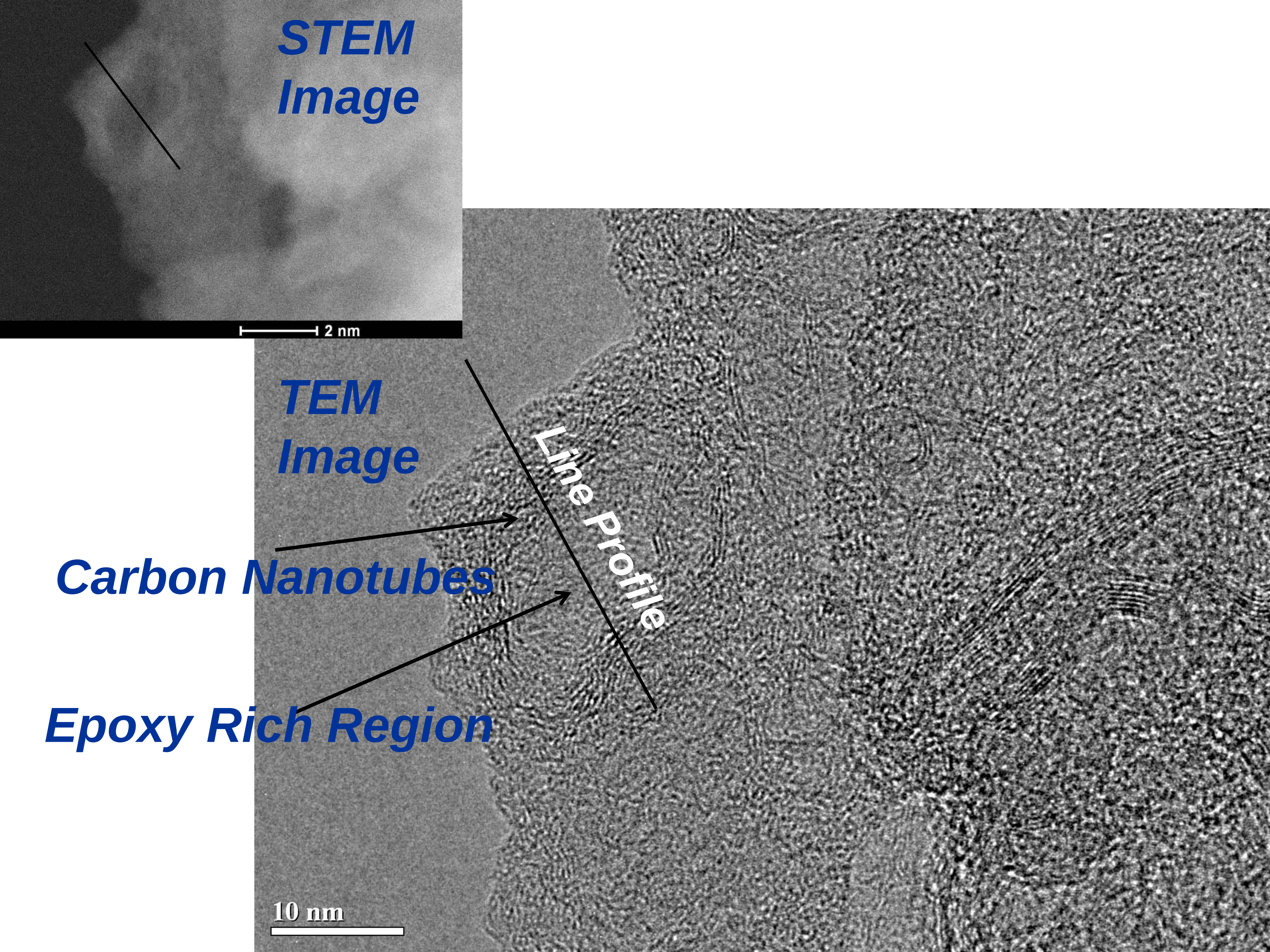
  sigma transition ~ 27 eV

In diamond

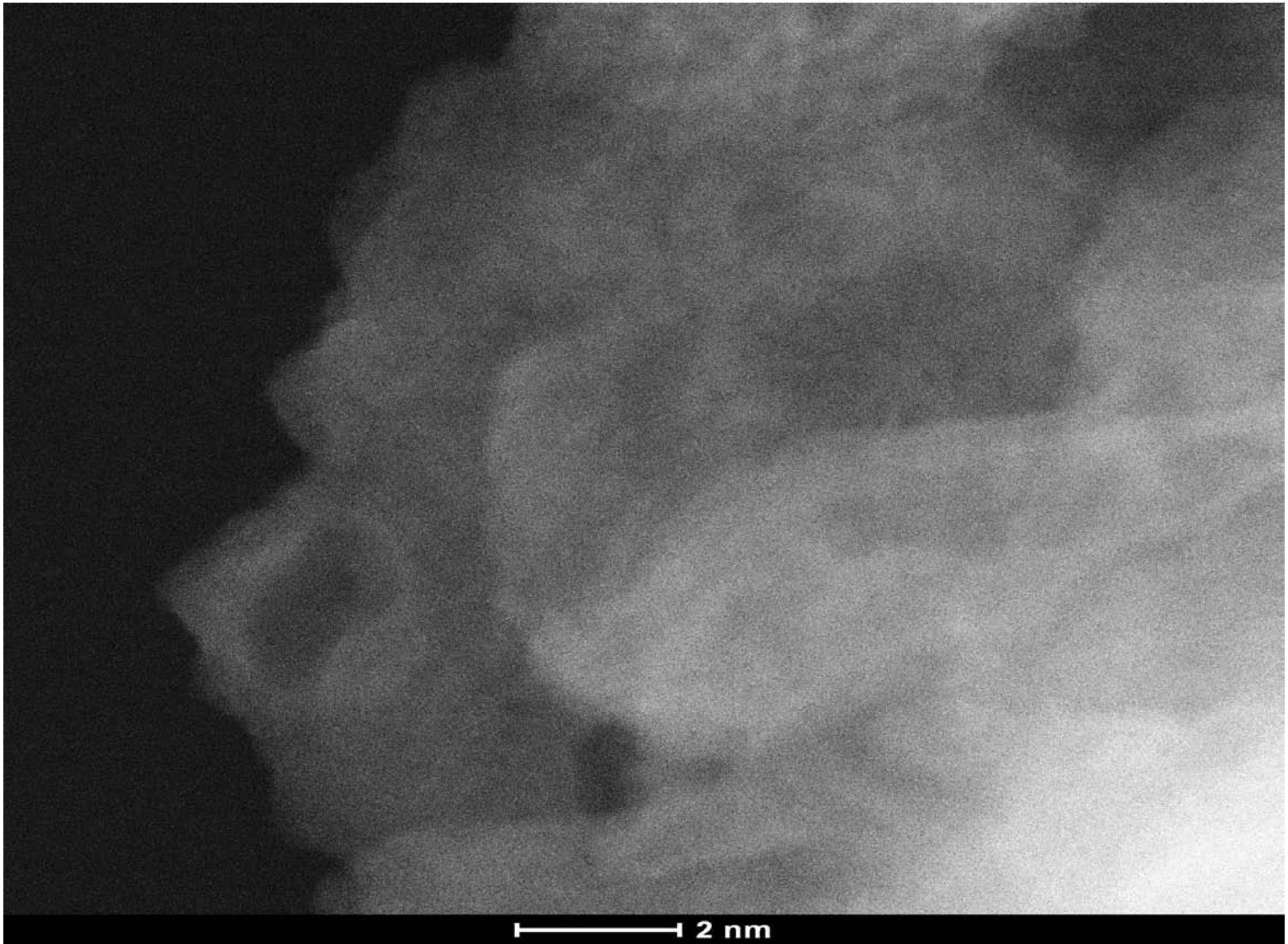
sigma transition ~ 34 eV

COOH Nanotubes in Epoxy Matrix

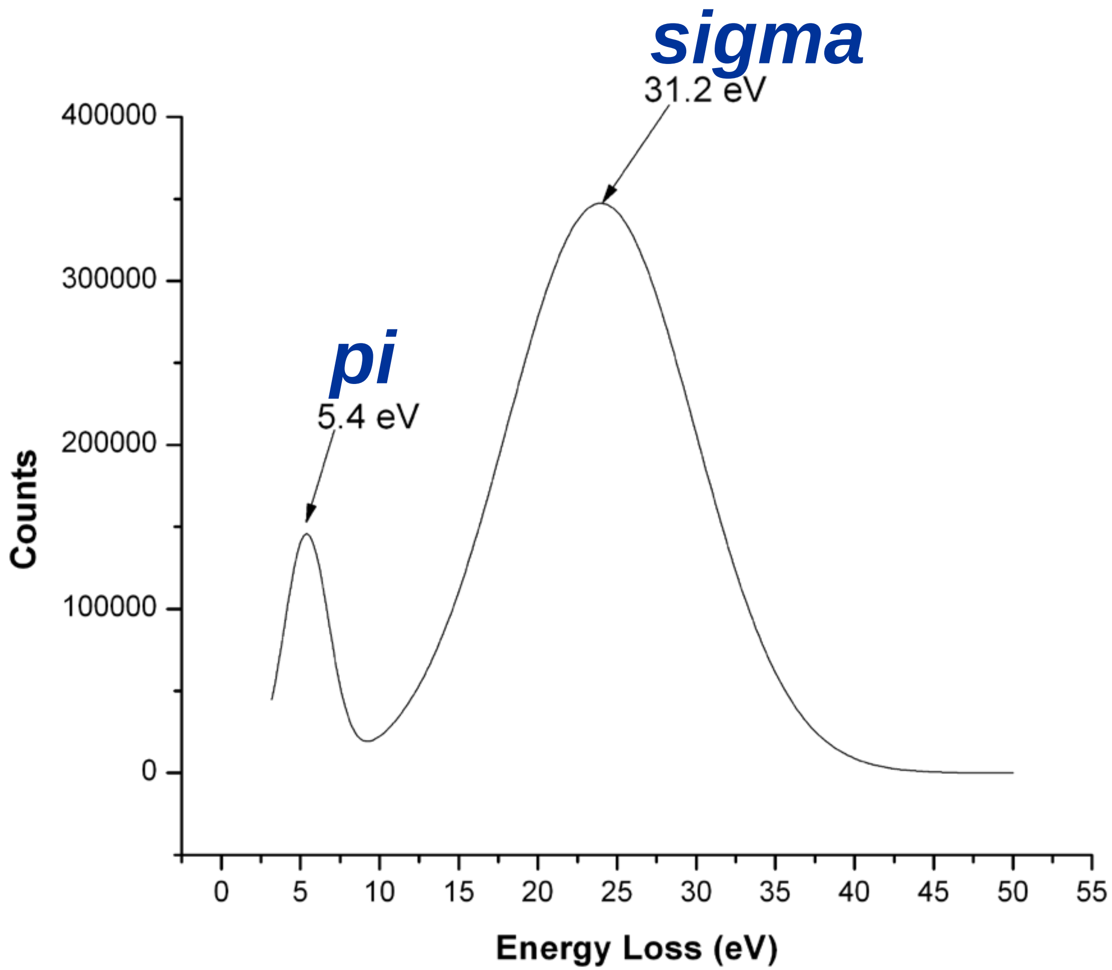



STEM
Image
2 nm
TEM
Image
Line Profile
Carbon Nanotubes
Epoxy Rich Region
10 nm

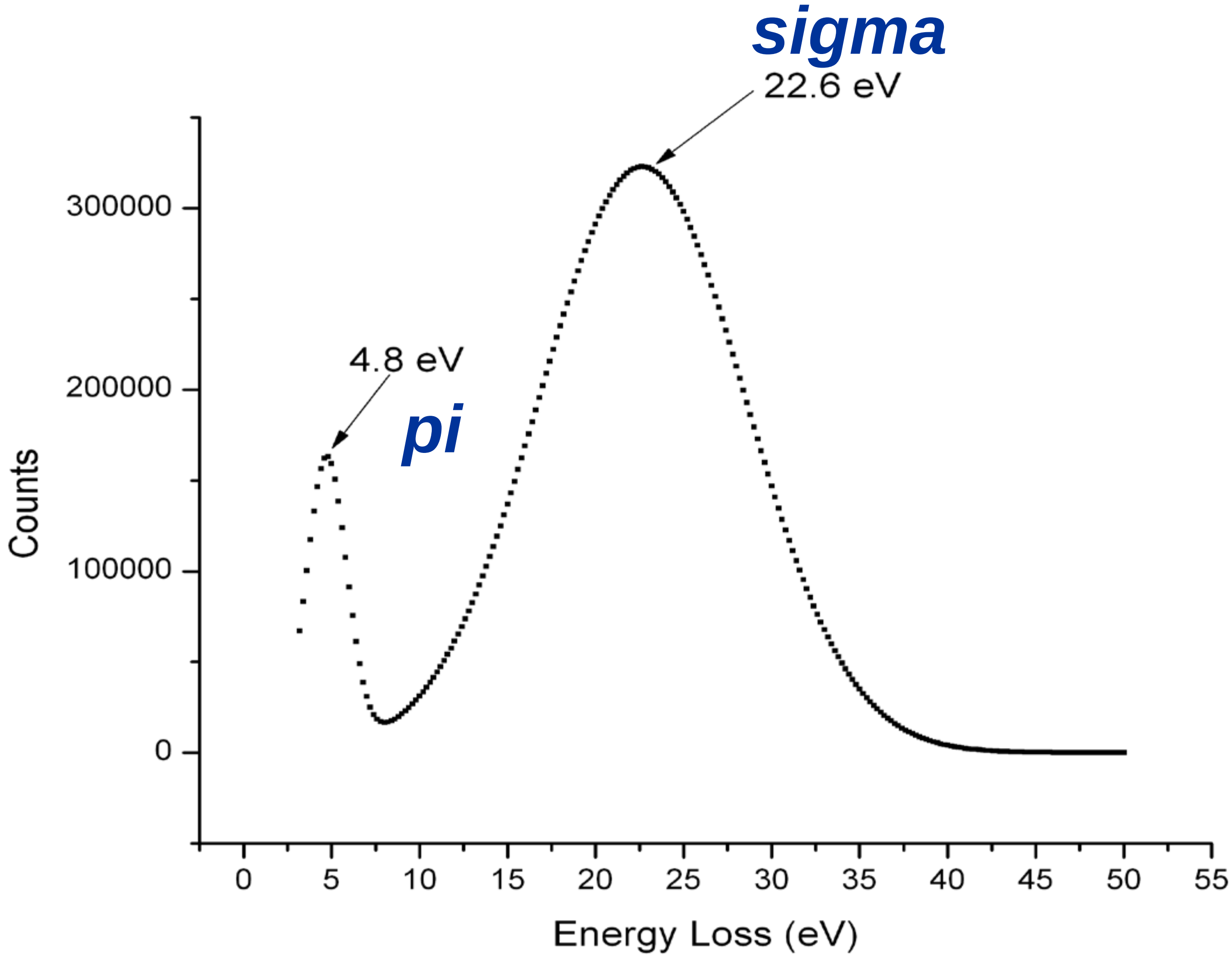
Post EELS Analysis



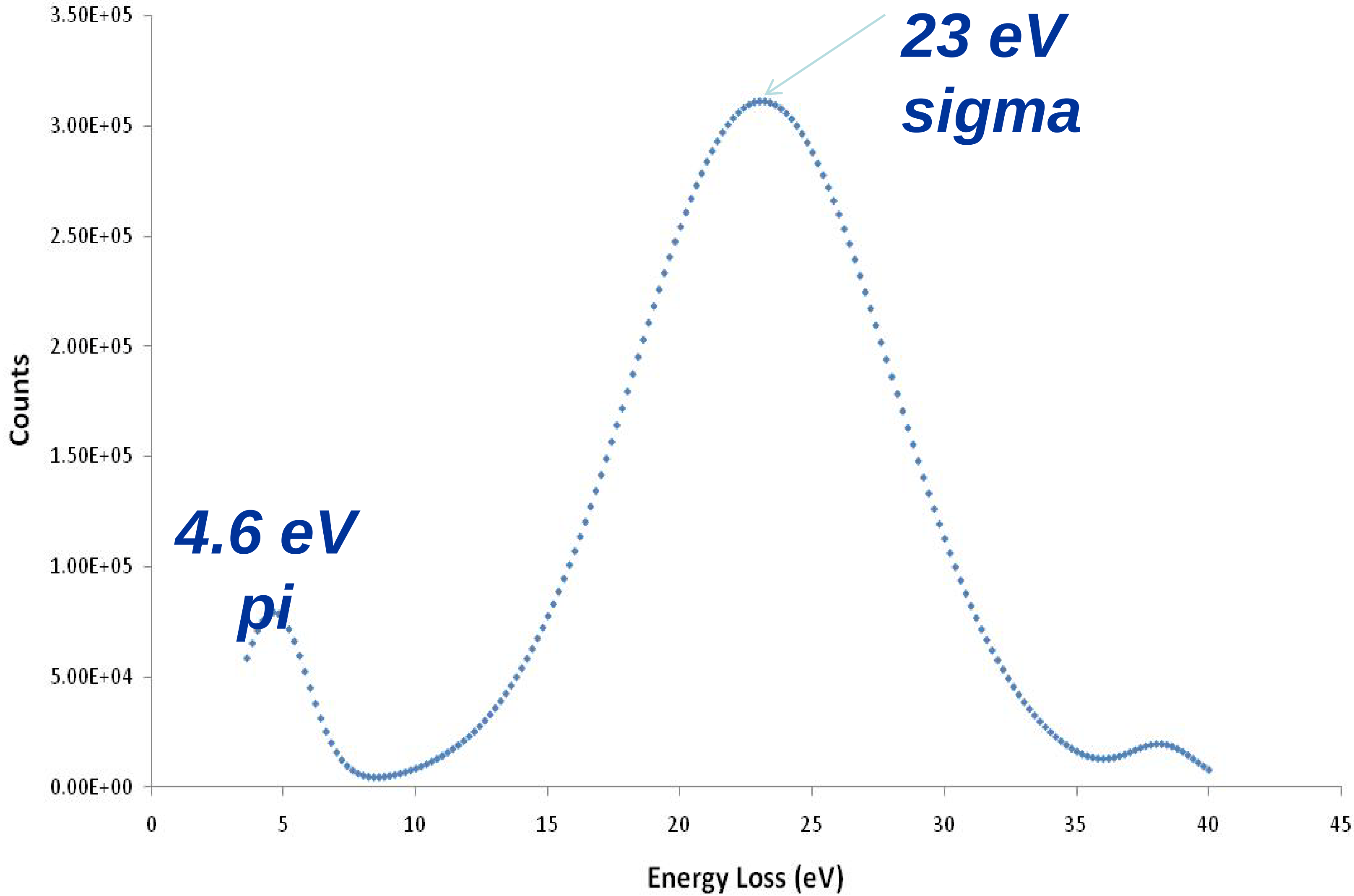
Nanotube EELS Spectra



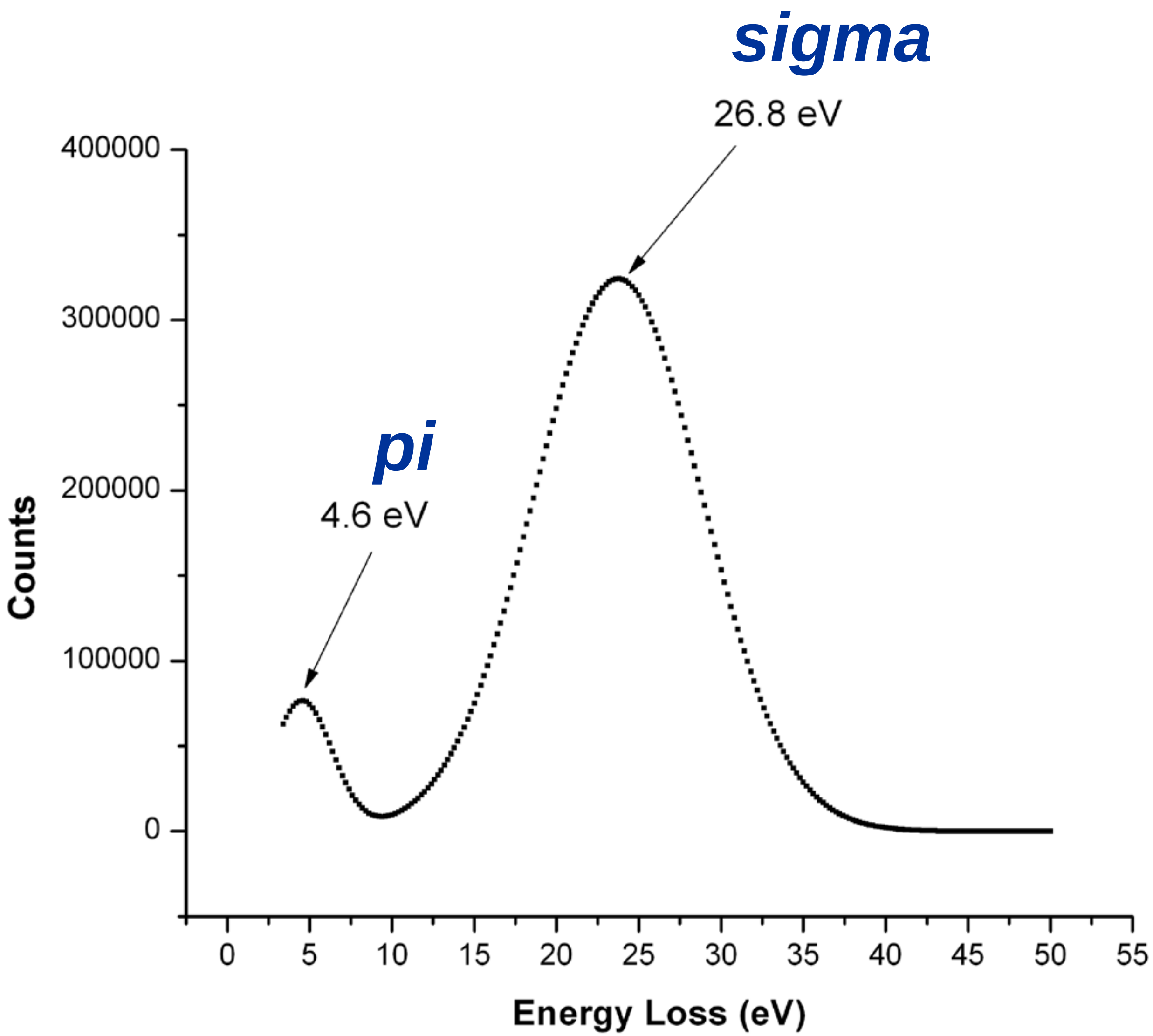
Epoxy EELS Spectra



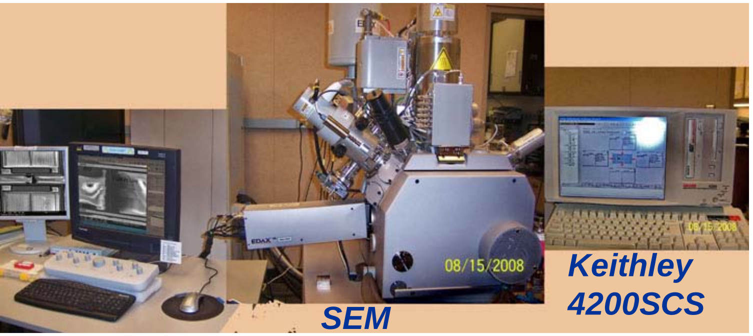
Pure Nanotube/Epoxy Interface EELS



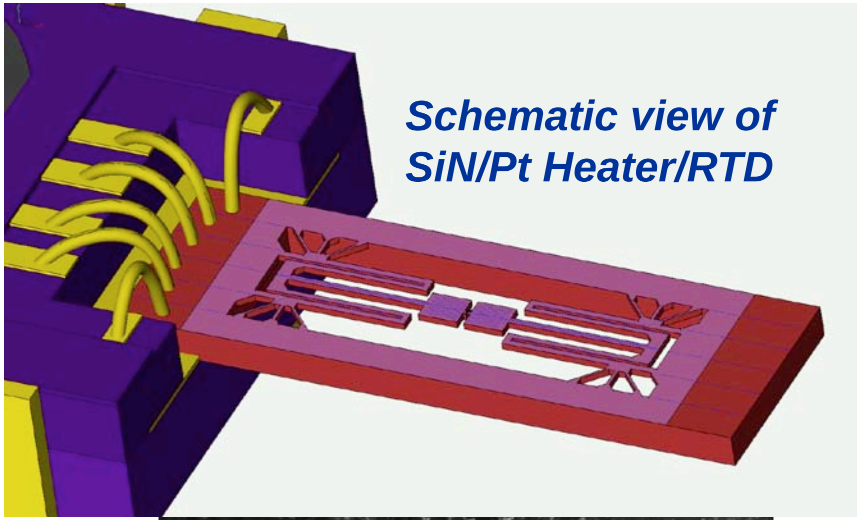
COOH Nanotube/Epoxy Interface EELS

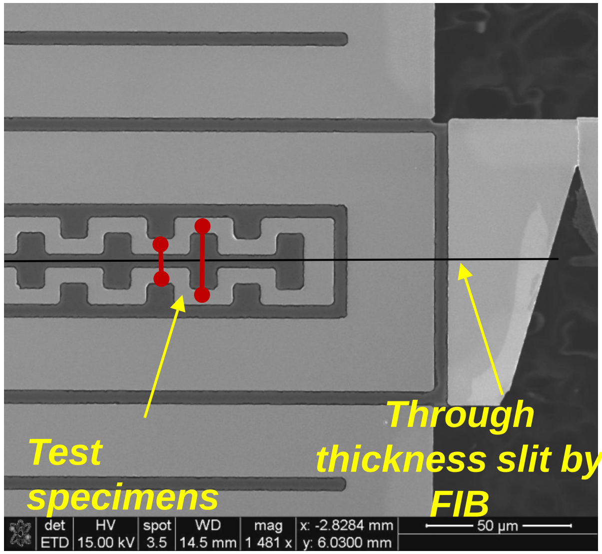


Sub-micron Scale Thermal Conductivity Measurement

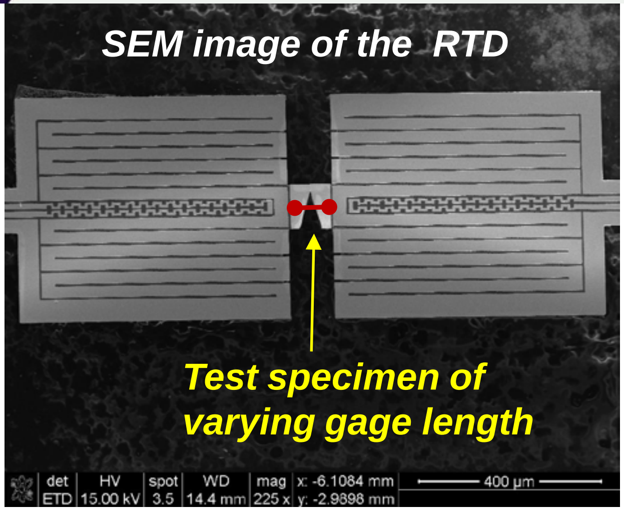


Resistance Temp Detector – RTD





Another test configuration using the RTD



Versatile RTD design for nano- to sub-micron scale direct thermal conductivity measurement

Summary

- Thermal transport mechanism in amorphous materials systems
  – Non bonded interaction provides the most energy to thermal transport in amorphous materials systems
  – Interface covalent bonding between polymers and nano constituents surfaces is a necessity for improving interface κ
- Phonon wave packet dynamics to visualize the phonon scattering & to calculate the transmission function in meso scale heat transfer